

Inhibited Al diffusion and growth roughening of Ga-coated Al (100)

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Abstract

Ab initio calculations indicate that the ground state for Ga adsorption on Al (100) is on-surface with local unit coverage. On Ga-coated Al (100), the bridge diffusion barrier for Al is large, but the Al→Ga *exchange barrier is zero*: the ensuing incorporation of randomly deposited Al's into the Ga overlayer realizes a percolation network, efficiently recoated by Ga atoms. Based on calculated energetics, we predict rough surface growth at all temperatures; modeling the growth by a random deposition model with partial relaxation, we find a power-law divergent roughness $w \sim t^{0.07 \pm 0.02}$.

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The role played by chemisorbed species in modifying energetics of and adatom diffusion on solid surfaces has recently come into focus in the field of epitaxial metal-on-metal growth. For example, the use of surfactants (agents inducing two-dimensional growth) has become common in recent years for metal surfaces, a classic case being that of Sb on Ag (111) (widely studied experimentally [1] and theoretically [2,3]): Sb adsorbates modify the nucleation behavior, island shapes, and ultimately the growth mode of Ag (111) via a repulsive interaction with Ag adatoms [2,3].

The changes in adatom diffusion and growth mechanisms that can be induced by surface contaminants may however be quite different: for instance, adsorbed species may turn the growth mode to three-dimensional instead. In this Letter we present one such “reverse surfactant”: a one-layer Ga coating inhibits Al diffusion on Al (100), and causes growth roughening, independently of temperature (i.e. diffusion related) effects.

Our predictions are based on ab initio theoretical results on Ga adsorption and Al/Ga coadsorption on Al (100). Ga wets Al (100), and the Ga monolayer adsorbed therewith on Al induces an anomalous diffusion mode for deposited Al adatoms: the barrier for Al→Ga *exchange* is zero. Thereby Al is embedded in the adsorbed Ga monolayer and its diffusivity drops to zero, while Ga floats to the surface with basically no barrier. The random incorporation of Al into the Ga coating layer realizes, at submonolayer coverage θ_{Al} , a percolation system with occupation probability $p = \theta_{\text{Al}}$. The growth mode of further layers is disordered (roughening) at all temperatures, due to the Ga-inhibited diffusion of Al adatoms and the concurrent efficient Ga recoating of the growing surface. Using a simple growth model we predict a power-law time divergence of the roughness, with exponent $\beta \sim 0.07 \pm 0.02$. In a different direction, our results suggest Al as a candidate substrate for the growth of thin-films of Ga in the dense phase Ga-III (unstable under normal conditions). Another reason of interest in this system is that liquid Ga embrittles Al, with (100) as the fracture plane [4].

Our ab initio total energy and force calculations are done within local density functional theory [5], using a plane-waves basis with a cutoff of 16 Ryd, fully-separable norm-

conserving pseudopotentials [6], and iterative diagonalization in a parallel implementation [7]. All geometries are fully optimized using Hellmann-Feynman forces. Metallic behavior is accounted for via a smeared occupation function with a smearing of 0.1 eV, and the first-order Methfessel-Paxton approximation to the δ function [8]. For all calculations, we use downfolded special \mathbf{k} -point meshes equivalent to the Chadi-Cohen [9] 10 points for bulk Al. These ingredients give a good descriptions of Al bulk and of the clean (100) surface [10].

Ga adsorption on Al (100) — The adsorption of Ga on Al (100) was studied at coverages between 1 and 1/4 in the fourfold-hollow on-surface and substitutional sites. The adsorption energy is defined in the standard way (see e.g. Ref. [2]). The adsorbate chemical potential is chosen to be the free-atom total energy [11]. The calculated adsorption energies, given in Table I, show that substitutional adsorption is favored over on-surface and subsurface sites by about 0.3 eV/atom at coverage $\theta_{\text{Ga}} \leq 1/2$ (i.e. whenever it is meaningful): the adsorbate prefers to sit *within* the surface layer, which implies surface segregation and surface confinement of Ga on Al (100) (compare with the analogous behavior of Sb/Ag (111) in Ref. [2]).

However, on-surface adsorption for *unit* Ga coverage is *energy-degenerate* with substitutional adsorption. The binding energy for on-surface Ga adsorption increases with increasing Ga coverage, and therefore there exists an *effective attraction between on-surface Ga adatoms*. The adatoms will tend to cluster and nucleate islands of local unit coverage even for $\theta_{\text{Ga}} < 1$. (This is opposite to the interadsorbate *repulsion* of Sb on Ag for all sites.)

Since thermal activation is needed (in the form of the creation of surface vacancies) for the substitutional adsorption mode to be actuated, at all temperatures sufficient to activate Ga diffusion on Al but not high enough to create surface vacancies the adsorption ground state will be the on-surface site. To estimate the temperature at which substitutional adsorption sets in, one must evaluate the relevant activation barrier. While it is relatively easy to calculate the formation *energy* of a surface vacancy (we find it to be 0.69 eV/vacancy at $\theta_{\text{vac}} = 1/4$), it is extremely difficult to accurately estimate the *barrier* against its formation. An intermediate configuration which is expected to be unavoidable at some stage of the

substitutional-Ga adlayer formation process is the adatom-vacancy Frenkel pair (a vacancy with the removed Al atom on the surface): its formation energy may then provide an estimate of the barrier in question. We calculated the pair formation energy to be 1.01 eV/defect at coverage 1/4. Assuming this energy as an estimate of the activation barrier, we infer that a temperature of $T_{\text{act}} \sim 450$ K is needed to activate one event per second (estimated as in Ref. [12], assuming a Boltzmann prefactor of 10^{-2} cm²/s, and a diffusion length of 50 bohr, which the ejected adatom is supposed to travel to get to a kink site; this corresponds to a reasonable step density of 10^{13} /cm²). According to this estimate, on-surface Ga adsorption will dominate at room temperature [13].

Anomalous Al diffusion on Ga:Al (100), and its consequences for the growth of Al — As surface diffusion is a crucial factor in epitaxial growth, and given the stability of a Ga monolayer on Al (100), it is natural to consider the way in which this surface coating affects the motion of Al adatoms. The bridge and exchange diffusion paths were studied for Al on Ga-contaminated Al (100) for $\theta_{\text{Ga}}=1$ and adatom coverage of $\theta_{\text{Al}}=1/9$ [14]. The barrier for the bridge transition state is 0.63 eV. However, for the transition state of the exchange reaction [12,15] between Al and Ga, we find a barrier which is zero within computational accuracy. The final state of the exchange process (Ga on-surface and Al embedded into the Ga monolayer) is favored by 0.29 eV with respect to the initial state (Al on-surface on the intact Ga monolayer). The adatom is thus incorporated within the Ga monolayer with no need for thermal activation, and a Ga atom concurrently pops up onto the surface. At low temperature, the Al→Ga exchange process is essentially irreversible, and the mobility of the Al atom embedded into the Ga adlayer is expected to be negligible: thus the Al adatom becomes immobile and its diffusivity drops to zero. While unexpected in general, a drop in diffusivity as the diffusion barrier gets lower is justified in this case by the asymmetry (Al-Ga) of the process [16].

The exchange process amounts to an individual segregation event for Ga: the absence of a barrier implies that Ga will efficiently float to the surface despite the moderate energy gain obtained therewith. The calculated adsorption energetics (Table I) for the substitutional

and sublayer sites indicates that segregation of Ga will be complete even at higher θ_{Al} . This is further confirmed (in addition to the above-mentioned 0.3 eV/atom gain upon Al→Ga exchange at $\theta_{\text{Ga}}=1$ and $\theta_{\text{Al}}=1/9$) by (a) a 0.3 eV/atom gain forming an on-surface Ga monolayer on perfect Al (100) from a mixed $\text{Ga}_{0.5}\text{-Al}_{0.5}$ surface alloy bilayer, (b) a 0.4 eV/atom gain upon Al→Ga exchange at $\theta_{\text{Ga}}=1/4$ and $\theta_{\text{Al}}=1/4$ [13]. Since Ga efficiently recoats the surface (see below), the Al→Ga exchange barrier should not depend appreciably on Al coverage, so Ga segregation is always very efficient.

The deposited Al adatoms exchange with Ga atoms from the wetting adlayer with essentially no diffusion prior to incorporation, a diffusion-unbiased hit-and-stick process. This process leads to the formation of a high-areal-density array of small (mostly monoatomic at low coverage), randomly-distributed Al clusters embedded within the Ga surface layer. If we formally view the Ga adlayer as an empty square lattice, upon deposition of a fraction θ_{Al} of an Al submonolayer the sites of this lattice are randomly occupied by Al adatoms with a probability $p=\theta_{\text{Al}}$. A percolation system is thus realized whose site occupation probability is equal to (and tunable via) the Al coverage. Using the standard results for site percolation on a two-dimensional square lattice [17], below the percolation-threshold coverage $\theta_{\text{Al}}^c \equiv p_c = 0.593$ the Al clusters are finite and have a fractal dimension $D\sim 1.2$, becoming $D\sim 1.9$ at p_c . Above p_c , the percolating clusters have Hausdorff dimension 2. This system may open interesting new possibilities, as for instance the direct study of percolation clusters and of tracer diffusion on a fractal cluster.

The growth of further layers is expected to proceed in a disordered fashion and roughening occurs with essentially no temperature dependence. Let us first assume that the Ga atoms kicked off the wetting layer are removed from the surface. While Al adatoms diffuse normally on previously-created Al areas, they are embedded instantaneously in the surface layer upon entering Ga-covered areas, which effectively act as drains for Al adatoms. This diffusion mode is equivalent to downstep diffusion with zero step barrier. Two-dimensional growth of the first layer follows immediately. Of course, however, the Ga atoms substituted for by Al adatoms remain on the surface. These Ga atoms diffuse rapidly on the Ga-covered areas,

they are attracted onto the previously created Al regions, and recoat them. This is because (a) Ga is less bound to Ga/Al(100) than to Al(100) by 0.2 eV, and (b) the bridge diffusion barrier for Ga on Ga:Al(100) is as low as 0.01 eV at $\theta_{\text{Ga}}=1$ [4], which we expect to hold qualitatively at lower coverage too, given the lower binding energy to the substrate (point (a)). Since Al adatoms do not diffuse and deposition is random, further incoming Al's will be embedded with equal probability within the newly created Ga overlayers ("second-level" Ga) as on the pristine Ga layer. New Al clusters will "nucleate" (by Al-Ga exchange) on top of previously embedded Al clusters as well as on pristine Ga areas. This process is analogous to overgrowth on an incomplete layer, so that three-dimensional growth ensues. This is all the more likely when the shape of the Al clusters is reasonably regular, i.e. for θ_{Al} above the percolation threshold p_c (where clusters have $D = 2$ and a relatively regular shape). In a sentence, the surface is coated with a diffusion-inhibiting segregating agent, causing growth roughening. For the latter to occur, the only condition is that Ga diffusion be activated so as to allow recoating of the Al clusters. As discussed above, this is a rather weak condition indeed; also, it is in fact immaterial at low temperature, because the substituted Ga will hardly leave at all the vicinity of its original site.

The hit-and-stick deposition mode emerging from the results discussed above leads to Poisson growth, with a roughness diverging in time as $t^{1/2}$. However, one should account for the fact that below and around the percolation threshold $\theta_{\text{Al}}^c = p_c$ the surface-embedded Al clusters are fractals, and their shape (and that of the "second level" Ga recoating areas) is highly irregular. Thus diffusion of Al down the highly ramified second-level Ga clusters may take place before exchange does. In view of this fact we model the growth of the system by random deposition with *partial relaxation*: adatoms stick where they land, except on the thinnest (one-atom wide) second-level Ga islands and at island edges: in practice, they move from the landing site to a nearest-neighbor site if the latter is lower in height, and stick there. We analyzed the statistical properties [18] of our partial relaxation model by 2+1-dimensional lattice simulations: the results indicate a roughness diverging in time as a power law, $w \sim t^\beta$, with $\beta \simeq 0.07 \pm 0.02$ [19]. This agrees with the finiteness of the range of

lateral correlations. The interesting point is that since the model seems fairly realistic for this system, it could possibly be experimentally tested. A more detailed statistical analysis will be given elsewhere.

Al as substrate for Ga growth — The general features of the Ga/Al system correlate with the size differences of Ga and Al in dense bulk phases. Ga is slightly larger than Al, and the two metals do not form high-density (nor other) alloys. This is compatible with both surface segregation with a moderate energy gain, and with the small in-plane lattice mismatch $m = [a_{\text{Ga}}/a_{\text{Al}} - 1]$ of Ga to Al. Fcc Ga (for which $m \sim 1.5\%$) distorts spontaneously into face-centered tetragonal Ga-III [20], whose mismatch to Al (100) is $m \sim -1.7\%$. These values are small enough to make pseudomorphic wetting of Ga on Al (100) favorable; so, geometry-wise, the stability of the Ga monolayer adsorbed on Al (100) seems just natural.

Our calculated surface energy of Ga:Al(100) at $\theta_{\text{Ga}} = 1$ is $0.12 \text{ eV/atom} = 24 \text{ meV/\AA}^2$ assuming the bulk energy of Ga-III (energy-degenerate with fcc Ga) as Ga chemical potential. This is much lower than the calculated [20] surface energy of Ga-III ($0.56 \text{ eV/atom} = 74 \text{ meV/\AA}^2$): this gain in surface energy suggests the use of Al (100) as substrate for thin-film growth of Ga-III. Assuming volume conservation, Ga-III accommodates its small in-plane lattice mismatch to fcc Al with a mere 3.5% expansion along the growth direction, so that pseudomorphic growth may be sustained up to appreciable thicknesses. It was shown recently [20] that the (100) surface of the stable α -Ga phase reconstructs so as to expose a Ga-III-like surface bilayer, so that the *surface* structure of Al-epitaxial Ga should remain Ga-III-like at all film thicknesses. However, dimerization of the Ga film into the α -phase structure above some critical thickness cannot be ruled out. These issues will be discussed elsewhere.

Low barrier for exchange: an estimate — The low cost of the Al \rightarrow Ga exchange may be explained similarly to Al-Al exchange on Al (100) (each atom involved is always at least three-fold coordinated, while at a bridge saddle point the adatom is only two-fold coordinated [15]). The bond lengths and adsorbate heights at the exchange saddle point (see Table II)

support this view: the exchanging-atoms dimer burrows about 4% deeper into the surface layer than in the Al-Al exchange on Al(100); also, not only does the exchanging Al adatom form short bonds to the three neighboring top-layer Ga atoms, but it is also *already bound to a second-layer Al*, forming a bond 2% shorter than bulk ones (about the same holds for the exchanging Ga). The overall number of bonds is 9 in the Al→Ga exchange, against 6 of the Al→Al exchange on clean Al. The initial and final states have a total of 12 bonds in both cases. A bond-cutting model allowing for bond saturation at high coordination [21], gives a gain of ~ 0.4 eV for a reduction of the number of cut bonds from 6 to 3, matching the ~ 0.3 eV difference of exchange barriers for clean Al [12,15] and Ga:Al(100). Coordination models often give inaccurate barrier values for different diffusion processes (the model above predicts a barrier of 0.9 eV for both exchange and bridge diffusion, the calculated [12,15] values being 0.3 eV and 0.6 eV), but one expects error cancellation when estimating a difference between barriers of two very similar processes (as done here [22]), so the agreement is probably not accidental.

Summary — Ga adsorption on Al (100) has a degenerate ground state: on-surface adsorption of local coverage unity at all temperatures, and thermally activated (above $T \sim 450$ K) substitutional adsorption at low coverage. The diffusion barrier for Al on Ga-coated Al (100) ($\theta_{\text{Ga}}=1$) is found to be large for bridge diffusion, but null for the Al→Ga exchange process, in which Al gets locked into the surface layer while Ga jumps onto the surface. Al is incorporated immediately upon deposition, while Ga efficiently segregates to the surface. At submonolayer Al coverage, Al incorporation in the Ga adlayer effectively realizes a percolation system, which is recoated by Ga as the growth proceeds. The surface grows rough, with a power-law diverging roughness $w \sim t^{0.07 \pm 0.02}$; this agrees qualitatively with the strong diffusion-inhibiting action of the Ga coating. Finally, we suggest that Al may be a good substrate for thin-film growth of metastable Ga-III.

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is somewhat tricky. In the whole span from deposition start to size saturation, the data may also be crudely fit by $\log w \sim 0.09 \log t - 0.01 (\log t)^2$. This is close to a simple power law, with a slightly different exponent. Roughness evolution data were obtained as averages over 100 runs of 3000 steps on a 200×200 lattice.

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TABLES

θ	1/4	1/2	1
$E_{\text{ad}}^{\text{subst}}$	3.83	3.82	—
relax	+3.0	+4.0	—
W	4.43	4.04	—
$E_{\text{ad}}^{\text{on-srf}}$	3.52	3.48	3.80
relax	-7.0	-11.6	+4.9
W	4.53	4.49	4.57
$E_{\text{ad}}^{\text{subsurf}}$	3.59	3.57	3.57
relax	-1.1	+1.3	-0.1
W	4.39	4.18	4.41

TABLE I. Adsorption energies (eV), adatom relaxations (percentage of interlayer distance), and work function (eV) for Ga on Al (100) in the on-surface, substitutional, and subsurface sites (see text for details).

Atom pair	This work	Ref. [12], Al:Al(100)
$h_{\text{Al}_{\text{ex}}}$	1.08	1.40
$h_{\text{Ga}_{\text{ex}}}$	1.15	
dimer length	4.77	4.84
$\text{Al}_{\text{ex}}\text{-Ga}_{\text{sub}}$	4.70	4.75
$\text{Al}_{\text{ex}}\text{-Al}_{\text{sub}}$	5.20	
$\text{Ga}_{\text{ex}}\text{-Ga}_{\text{sub}}$	4.57	
$\text{Ga}_{\text{ex}}\text{-Al}_{\text{sub}}$	5.21	

TABLE II. Bond lengths and heights (bohr) for Al→Ga exchange on Ga:Al(100). Bond length in bulk Al: 5.30 bohr. X_{ex} are exchanging atoms, X_{sub} substrate. Right column: values for Al-Al exchange on Al (100) (only Al's involved).